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                POLYATOMIC PHOTODISSOCIATION DYNAMICS.(U)
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Title: Polyatomic Photodissociation Dynamics 394-013

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Polyatomic Photodissociation Dynamics

During the contract period photofragment spectroscopy studies of several small halide molecules were carried out. In two cases evidence for novel free radical dissociation processes was found.

1) Methylene iodide (CH_2I_2). When photolyzed at a wavelength of 266nm direct evidence for the following dissociation pathway was seen:

$$CH_2I_2 + h\nu \rightarrow CH_2I + I.$$
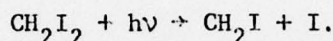
The fragments were found to carry a very high fraction (85-90%) of excess energy in internal excitation, most likely in the form of ro-vibrational excitation of the CH_2I species. While this result is consistent with a simple statistical model for energy partitioning, the fragment angular distribution indicates parent molecule breakup occurs very quickly on a rotational timescale, so that a statistical decay is unlikely. A simple direct impulsive model, which treats the carbon atom as loosely bound to the rest of the radical and requires momentum conservation as the carbon atom recoils from the I atom, predicts an internal excitation of 84% of available energy, in good agreement with experiment.

A second dissociation process was observed, yielding CH_2 fragments with surprisingly high translational energy. The lowest energy assumption, that the process is

$$CH_2I_2 + h\nu \rightarrow CH_2 + I_2,$$
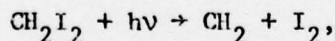
was found to be inconsistent with the generally accepted value (91 kcal mole^{-1}) of the heat of formation of CH_2. If the above process were occurring, the observed photofragment energetics would place an upper limit to the heat of formation of CH_2 of 40 kcal mole^{-1}. Two possible explanations were considered: photodissociation of a dimeric species in the molecular beam and a two photon dissociation process. The former was ruled out by experiments at elevated molecular beam temperatures, the latter was presumably excluded by the observed linear dependence of CH_2 signal on laser intensity. However, if the second photon absorption

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has a very large extinction coefficient, this dependence would appear linear except at very low laser intensities, where poor signal-to-noise ratios make accurate measurements impossible. The existence of a second absorption was proven by measuring CH_2I signal as a function of laser intensity. This dependence shows a strong saturation at relatively low light levels, indicating some photon-dependent depletion process is occurring. Thus there must be a sequential two photon absorption, in which an initially formed CH_2I radical absorbs a second photon and dissociates to $CH_2 + I$. The detailed dynamics of this radical dissociation process are still not understood. Theories of two photon angular distributions will be applied to the data to determine the extent of correlated dynamics in the three-body dissociation system.

2) Acetyl iodide (CH_3COI). As expected, the primary photodissociation process in acetyl iodide at 266nm is C-I bond breakage and recoil of an I atom fragment. However, the excess available energy above that needed to break the C-I bond is sufficient to further decompose the acetyl fragment to CO and CH_3. In fact, no evidence for a recoiling acetyl fragment could be found. Photofragment spectra of both CO and CH_3 were observed, but could conceivably have arisen from dissociation of an acetyl fragment in the detector's electron bombardment ionizer. To test this, the spectra can be transformed to recoil translational energy distributions. If both CH_3 and CO signal originated from a recoiling CH_3CO radical, their energy distributions would be identical, and would match that observed for the I atom fragment. This was not the case. Also, the angular distributions for CO and CH_3 are more isotropic than for I, indicating something more complex than a simple two-body breakup is occurring.

Acetyl iodide thus provides another example of a radical dissociation process, initiated by the impulsive energy release during C-I bond breakage. The simplest dynamical model might predict the primary initial excitation of the acetyl radical to be in the CCO bending mode, yet dissociation must occur from a radical highly excited in the C-C stretching vibration. Thus the radical might live for many vibrational periods, undergoing statistical redistribution of its excess energy prior to decomposing via a classic unimolecular decay process. Further theoretical work on three body kinematics will be needed to tell if this,

rather than instantnaeous decomposition, is happening. The results
should prove useful to an understanding of intramolecular energy transfer
processes.

3) Tin tetrabromide ($SnBr_4$). A clear example of statistical unimolecular
decay of photoexcited species was found in the ultraviolet photodissocia-
tion of $SnBr_4$. Fragment recoil translational energy distributions peak
at or near zero and have an exponential fall-off, exactly the behavior
expected for classical unimolecular decomposition. Statistical decay
is the heart of many reaction rate theories, yet experimental verification
of its theoretical aspects has not been easy. Crossed molecular beam
reaction and ionic dissociation studies have provided some input, but
have been complicated by large and sometimes ill-defined distributions
in kinematic parameters such as angular momentum and excess internal
energy. Photodissociation, on the other hand, offers a "cleaner"
experimental test, since the angular momentum of the complex is known
(just the thermal momentum of the parent molecule) and the excess energy
(photon energy minus bond strength) is known, has a narrow distribution,
and can be systematically varied via wavelength selection. Analysis of
photofragment spectra should provide insight into such basic aspects
of unimolecular decay theories as determining the effective number of
oscillators and the role of zero point energy.